

AD624017

PREDICTING THE INTERGRANULAR CORROSION
OF AUSTENITIC STAINLESS STEELS

Technical Report No. 3

To

Office of Naval Research

Contract Number Nonr - 591(17)

W. D. France, Jr.

N. D. Greene

Rensselaer Polytechnic Institute

Troy, New York

October, 1965

CLEARINGHOUSE FOR FEDERAL SCIENTIFIC AND TECHNICAL INFORMATION			
Hardcopy	Microfiche		
\$ 2.00	\$ 0.50	29 pp	as
ARCHIVE COPY			

DEC 2 1965

PREDICTING THE INTERGRANULAR CORROSION
OF AUSTENITIC STAINLESS STEELS

W. D. France, Jr.

N. D. Greene

Corrosion Research Laboratory
Materials Research Center
Rensselaer Polytechnic Institute
Troy, New York

Presented at the 21st NACE Conference,
St. Louis, Missouri, March 15-19, 1965

ABSTRACT

The precise environmental conditions necessary for the intergranular corrosion of austenitic stainless steels have been determined by potentiostatic methods. Intergranular corrosion of sensitized 18Cr - 8Ni stainless steel only occurs in limited potential regions. These results have been used to develop a new method for rapidly predicting the intergranular corrosion tendencies of various sulfuric acid environments. It is also shown that sensitized stainless steels may be used in many media without the occurrence of intergranular attack.

(1)
The Chromium Depletion Theory has been successfully employed to predict numerous measures for preventing the intergranular corrosion of austenitic stainless steels. Examples include solution quenching, stabilization with titanium and niobium additions and the use of low carbon alloys.⁽²⁾ Although very useful, this theory has a serious flaw: it specifies the necessary but not sufficient conditions for intergranular attack. A continuous grain boundary precipitate of chromium-rich carbide is considered necessary for intergranular corrosion.* However, many environments do not selectively attack the grain boundaries of sensitized stainless steels,^(5,6) and the use of costly preventative measures is unnecessary. Thus, knowledge of the environmental conditions which cause intergranular attack would permit more efficient and economical application of

* This is not completely accurate, since intergranular corrosion of austenitic stainless steels have been observed in the absence of grain boundary carbide precipitates (3,4). These observations are limited to very specific environments, and thus, the Chromium Depletion Theory can be considered generally correct.

austenitic stainless steels.

Recent electrochemical studies⁽⁵⁻⁹⁾ have demonstrated that the intergranular corrosion of austenitic stainless alloys occurs only in limited potential regions. If these regions were precisely and completely characterized, it would be possible to predict, a priori, whether a given environment will cause intergranular attack on the basis of a corrosion potential measurement.

The purpose of this investigation was to precisely determine the potential dependence of intergranular attack, and to test the possibility of predicting the occurrence of this type of attack in various environments. Sulfuric acid solutions were chosen for this study since stainless steels are frequently employed in such media.

EXPERIMENTAL

A cast, austenitic stainless steel of the CF-8 type was used for most experiments since the large grain size facilitated visual observation of intergranular attack. Nickel content was slightly above normal specifications to insure absence of ferrite phase. Wrought Type 304 stainless steel was also included for comparison purposes. The compositions of these two alloys are listed in Table I.

Rectangular specimens with an area of approximately 7 cm^2 were water quenched after one hour at 1100°C (2000°F) and sensitized by heating at 675°C (1250°F) for 25 hours. Specimens were ground to 00 emery finish, and their dimensions were measured within $\pm 0.001 \text{ cm}$. Prior to testing, samples were degreased in boiling benzene, rinsed with doubly distilled water, dried and weighed to the nearest 0.1 mg. All solutions were prepared from reagent grade chemicals and doubly distilled water.

Two types of corrosion tests were employed: controlled potential and conventional weight loss measurements. A controlled potential corrosion test is similar to a conventional test except specimen potential is maintained constant with a potentiostat^(10,11). All tests were conducted in a polarization cell described elsewhere⁽¹¹⁻¹³⁾. This facilitated measurement and control of specimen potential which was measured relative to a saturated calomel electrode (S.C.E.) with a Luggin-Haber probe. Temperature was thermostatically controlled within $\pm 1^\circ\text{C}$.

Corrosion test duration depended on the severity of attack with a maximum period of 100 hours. Extended tests up to 1000 hours yielded results nearly identical to those

obtained during 100 hours. After testing, specimens were dried, weighed and examined microscopically. To detect fine grain boundary attack, specimens were plastically deformed before visual examination.

Controlled potential corrosion tests were conducted in pure 1, 5 and 10 normal sulfuric acid at 25°, 40° and 90°C at various potentials maintained within ± 10 mv. Conventional corrosion testing was performed in these same media with and without oxidizer additions (Ce^{+4} , Fe^{+3} , and Cu^{+2}). In some corrosion tests, specimens were galvanically coupled to platinum or copper.

RESULTS

Controlled Potential Tests

Intergranular corrosion only occurs in specific potential regions as shown in Figures 1-3. For convenience, the observed attack is divided into three categories: general corrosion, fine intergranular corrosion, and coarse intergranular corrosion.* Interpolation between points has been used to map zones of intergranular attack, which enlarge with acid concentration and temperature. Tests with sensitized

* Examples of these three categories are illustrated in Figures 7-9, respectively.

Type 304 stainless steel (Table II) yielded nearly identical results.

Overall corrosion rates calculated from weight loss are plotted in Figures 4-6. These data indicate average overall rates rather than true penetration, since intergranular attack is present in some cases. These curves are very similar to those obtained by potentiostatic anodic polarization.^(14,15) This is expected since applied anodic current closely approximates actual corrosion rate.^(16,17)

Comparisons of Figures 1-3 with Figures 4-6 shows that susceptibility to intergranular corrosion begins at approximately the maxima of Figures 4-6. This demonstrates that selective grain boundary attack is restricted to the passive and transpassive regions and does not occur in the active state in these media.

Conventional Corrosion Tests.

Results of these tests, conducted in sulfuric acid with and without oxidizer additions, are tabulated in Table III. Corrosion potentials were measured during testing and are also listed in the Table. The presence or absence of intergranular attack was predicted on the basis of these potentials and the data in Figures 1-3. There is complete agreement

between observed and predicted results. That is, controlled potential and conventional corrosion tests are directly comparable at constant potential, acid concentration, and temperature.

The correspondence between controlled potential and conventional corrosion tests is demonstrated more vividly by the detailed comparisons presented in Figures 7-9. Here, conventional corrosion tests are compared with controlled potential studies performed at similar potentials. These examples have been selected to show uniform (Figure 7), fine intergranular (Figure 8), and coarse intergranular (Figure 9) attack. In each case, both the type of attack and corrosion rate are almost identical. The correspondence of visual appearances is particularly striking. The slight discrepancies in corrosion rates are due to variations in potentials during the two types of experiments.

DISCUSSION

The above experiments demonstrate that both the rate and type of intergranular corrosion in a given environment are unique functions of electrode potential. Consistent with other studies,^(18,19) small amounts of non-complexing oxidizers such as ceric, ferric and cupric ions, only influence

electrode potential and do not alter dissolution behavior. Oxidizers which form complexes with iron, chromium or nickel (e.g., chlorine or chlorine-containing compounds) would preclude such predictions, since they strongly influence dissolution kinetics.

The above results and techniques would be useful in engineering applications to predict the intergranular susceptibility of a given environment. There are, however, several precautions which must be observed. First, the data presented in Figures 1-3 contains extrapolated points and may be influenced by time of sensitization. These data may be considered as representative of an extreme condition of sensitization which would be rarely achieved in normal practice. Although there is little difference between wrought and cast alloys of the 18Cr - 8Ni type, these results may not apply to other austenitic stainless steel alloys. Exposure time may also influence results and, of course, this should be determined before applying these methods to long term industrial exposure. However, 100 and 1000 hour corrosion tests yielded identical results and intergranular attack, when present, was usually visually apparent after 10-20 hours. Finally, it is necessary that corrosion

potentials remain in a region corresponding to general corrosion if intergranular attack is to be avoided. This may be difficult to achieve or control in some industrial processes where environmental conditions fluctuate widely. Aside from these practical problems, this investigation clearly demonstrates the accurate prediction of intergranular corrosion susceptibility of sulfuric acid solutions. Other media, such as phosphoric and acetic acids, could also be characterized by controlled potential corrosion testing. Each environment probably possesses unique characteristics, since Streicher⁽²⁰⁾ has shown that there is no correlation between intergranular susceptibility in different acid solutions at nearly constant potential.

Intergranular corrosion can be prevented by altering the environment as shown in Table III. Removing copper sulfate from normal H_2SO_4 at $90^\circ C$ (Test 18) prevents intergranular corrosion (Test 16). Also, anodic or cathodic protection could be employed to shift potential to a region of general corrosion. For example, stainless steel is immune to intergranular attack and corrodes at less than 2 mpy in $5N H_2SO_4$ at $90^\circ C$ in the potential range 0.40 to 0.60 volt vs. S.C.E. (Figures 3 and 6). This potential could be maintained by appropriate oxidizer concentration or by externally applied current.

SUMMARY

1. The intergranular corrosion of sensitized 18Cr-8Ni stainless steels in sulfuric acid media occurs in limited potential regions whose limits vary with acid concentration and temperature.
2. It is possible to rapidly predict the intergranular susceptibility of various sulfuric acid - oxidizer mixtures on the basis of corrosion potential measurements and controlled potential corrosion tests.

ACKNOWLEDGMENT

We thank the Office of Naval Research
for their support of this program;
Ohio State University and the Alloy
Casting Institute for supplying cast
stainless steel samples.

REFERENCES

1. E. C. Bain and R. H. Aborn, Trans. Amer. Soc. Steel Treat., 18, 837 (1930).
2. E. C. Bain, R. H. Aborn and J. J. Rutherford, Trans. Amer. Soc. Steel Treat., 21, 481 (1933).
3. C. Edeleanu, Chem. and Ind., 42, 1360 (1958).
4. M. A. Streicher, J. Electrochem. Soc., 106, 161 (1959)
5. E. Brauns and G. Pier, Stahl u. Eisen., 75, 579 (1955)
6. V. Cihal and M. Prazak, Hutnicke Listy, 11, 225 (1956).
7. L. Clerbois, F. Clerbois, and J. Massart, Electrochimica Acta, 1, 70 (1959).
8. H. J. Schuller, P. Schwaab and W. Schwenk, Archiv. fur das Eisenhüttenwesen, 33, 853 (1962).
9. W. Schwenk, H. J. Schuller, and P. Schwaab, Werkstoffe und Korrosion, 15, 621 (1964).
10. N. D. Greene, C. R. Bishop and M. Stern, J. Electrochem. Soc., 108, 836 (1961).
11. N. D. Greene, Experimental Electrode Kinetics, 1965, p.37. Rensselaer Polytechnic Institute, Troy, N. Y.
12. M. Stern, J. Electrochem. Soc., 102, 609 (1955).
13. M. Stern and A. C. Makrides, ibid., 107, 782 (1960).
14. C. Edeleanu, J. Iron Steel Inst., 188, 122 (1958).
15. N. D. Greene, Corrosion, 15, 369t (1959).
16. M. Stern and A. L. Geary, J. Electrochem. Soc., 104, 56 (1957).

17. N. D. Greene, Corrosion, 18, 136t (1962).
18. N. D. Greene, J. Electrochem. Soc., 107, 457 (1960).
19. J. M. Kolotyrkin, N. J. Bune and G. M. Florianovich,
Symposium Europeen sur les Inhibiteurs de Corrosion,
Universita degli Studi di Ferrara, Italy, 1961, p. 493
20. M. A. Streicher, Corrosion, 20, 57t (1964).

TABLE I
Stainless Steel Compositions
 (Weight Per Cent)

Cast Alloy (CF-8 Type)	Type 304
C.....0.08	C.....0.072
Mn.....0.74	Mn...0.60
Si.....1.22	P.....0.024
Cr...18.08	S.....0.014
Ni...12.20	Si...0.37
N.....0.05	Cr..18.75
Fe...Balance	Ni...8.65
	Mo...0.46
	Cu...0.30
	Co...0.22
	N.....0.032
	Fe...Balance

TABLE II

CONTROLLED POTENTIAL CORROSION TESTS

Sensitized Type 304 Stainless Steel

Environment	Potential (volts)	Immersion Time (hrs)	Corrosion Rate (mpy)	Observations
1N H ₂ SO ₄ at 25°C	0.300	100	0.9	General Corrosion
1N H ₂ SO ₄ at 25°C	-0.240	100	8.3	Fine IGA
1N H ₂ SO ₄ at 25°C	-0.280	98	33	Fine IGA, Grain dis- lodgement.
1N H ₂ SO ₄ at 90°C	0.940	100	230	Coarse IGA
1N H ₂ SO ₄ at 90°C	-0.150	43	3700	Coarse IGA, grain dis- lodgement.
1N H ₂ SO ₄ at 90°C	-0.200	18	7500	Coarse IGA, grain dis- lodgement

TABLE III

PREDICTING INTERGRANULAR CORROSION

Sensitized CF-8 Type Stainless Steel
(100 Hour Maximum Test Duration)

G: General Corrosion. IGA: Intergranular Attack

Test	Environment	Corrosion Potential-Volts vs SCE	Type of Corrosion	
			Predicted	Observed
1.	1N H ₂ SO ₄ at 25°C	-0.44 to -0.41	G	G
2.	1N H ₂ SO ₄ and Pt couple at 25°C	-0.31 to -0.29	G	G
3.	1N H ₂ SO ₄ plus 0.2 g/l CuSO ₄ .5H ₂ O and Pt couple at 25°C	-0.24 to -0.26	IGA	IGA
4.	1N H ₂ SO ₄ plus 0.3 g/l CuSO ₄ .5H ₂ O and Cu couple at 25°C	0.00 to 0.01	G	G
5.*	1N H ₂ SO ₄ plus 2.0 g/l CuSO ₄ .5H ₂ O at 25°C	0.22 to 0.26	G	G
6.	1N H ₂ SO ₄ plus 2.0 g/l Fe ₂ (SO ₄) ₃ .6H ₂ O at 25°C	0.30 to 0.54	G	G
7.	1N H ₂ SO ₄ plus 1.0 g/l Ce(SO ₄) ₂ .4H ₂ O at 25°C	0.87 to 0.94	G	G
8.	5 N H ₂ SO ₄ at 25°C	-0.41 to -0.36	G	G
9.	10N H ₂ SO ₄ at 25°C	-0.38 to -0.36	G	G
10.	10N H ₂ SO ₄ plus 1.0 g/l CuSO ₄ .5H ₂ O at 25°C	0.24 to 0.25	G	G
11.*	10N H ₂ SO ₄ plus 2.0 g/l Fe ₂ (SO ₄) ₃ .6H ₂ O at 25°C	0.59 to 0.61	G	G
12.	1N H ₂ SO ₄ plus 1.0 g/l CuSO ₄ .5H ₂ O at 40°C	0.14 to 0.18	G	G

Test	Environment	Corrosion Potential-Volts vs SCE	Type of Corrosion	
			Predicted	Observed
13.	1N H ₂ SO ₄ plus 0.5 g/l Ce(SO ₄) ₂ ·4H ₂ O at 40°C	0.92 to 0.93	G	G
14.	5N H ₂ SO ₄ plus 8.0 g/l Ce(SO ₄) ₂ ·4H ₂ O at 40°C	1.00 to 1.03	IGA	IGA
15.	10N H ₂ SO ₄ plus 5.0 g/l Ce(SO ₄) ₂ ·4H ₂ O at 40°C	1.04 to 1.06	IGA	IGA
16.	1N H ₂ SO ₄ at 90°C	-0.43 to -0.42	G	G
17.	1N H ₂ SO ₄ and Pt couple at 90°C	-0.37 to -0.36	G	G
18.	1N H ₂ SO ₄ plus 0.3 g/l CuSO ₄ ·5H ₂ O at 90°C	-0.06 to -0.34	IGA	IGA
19.	1N H ₂ SO ₄ plus 4.0 g/l CuSO ₄ ·5H ₂ O at 90°C	0.23 to 0.25	IGA	IGA
20.	1N H ₂ SO ₄ plus 10.0 g/l Ce(SO ₄) ₂ ·4H ₂ O at 90°C	0.92 to 0.95	IGA	IGA
21.	10N H ₂ SO ₄ plus 3.0 g/l CuSO ₄ ·5H ₂ O at 90°C	-0.34 to -0.32	G	G
22.	10N H ₂ SO ₄ plus 5.0 g/l Fe ₂ (SO ₄) ₃ ·6H ₂ O at 90°C	0.57 to 0.64	IGA	IGA
23.	10N H ₂ SO ₄ plus 5.0 g/l Ce(SO ₄) ₂ ·4H ₂ O at 90°C	0.99 to 1.03	IGA	IGA

* 1000 Hour Tests

FIGURES

Figure 1. Intergranular Corrosion of Sensitized Cast Stainless Steel in Sulfuric Acid at 25°C.

○: General Corrosion
◐: Fine Intergranular Corrosion
●: Coarse Intergranular Corrosion

Figure 2. Intergranular Corrosion of Sensitized Cast Stainless Steel in Sulfuric Acid at 40°C.

○: General Corrosion
◐: Fine Intergranular Corrosion
●: Coarse Intergranular Corrosion

Figure 3. Intergranular Corrosion of Sensitized Cast Stainless Steel in Sulfuric Acid at 90°C.

○: General Corrosion
◐: Fine Intergranular Corrosion
●: Coarse Intergranular Corrosion.

Figure 4. Potential vs Corrosion Rate of Sensitized Cast Stainless Steel in Sulfuric Acid at 25°C.

Figure 5. Potential vs Corrosion Rate of Sensitized Cast Stainless Steel in Sulfuric Acid at 40°C.

Figure 6. Potential vs Corrosion Rate of Sensitized Cast Stainless Steel in Sulfuric Acid at 90°C.

Figure 7. Comparison of Controlled Potential and Conventional Corrosion Tests. General Corrosion (100X).

Figure 8. Comparison of Controlled Potential and Conventional Corrosion Tests. Fine Intergranular Corrosion (100X).

Figure 9. Comparison of Controlled Potential and Conventional Corrosion Tests. Coarse Intergranular Corrosion (50X).

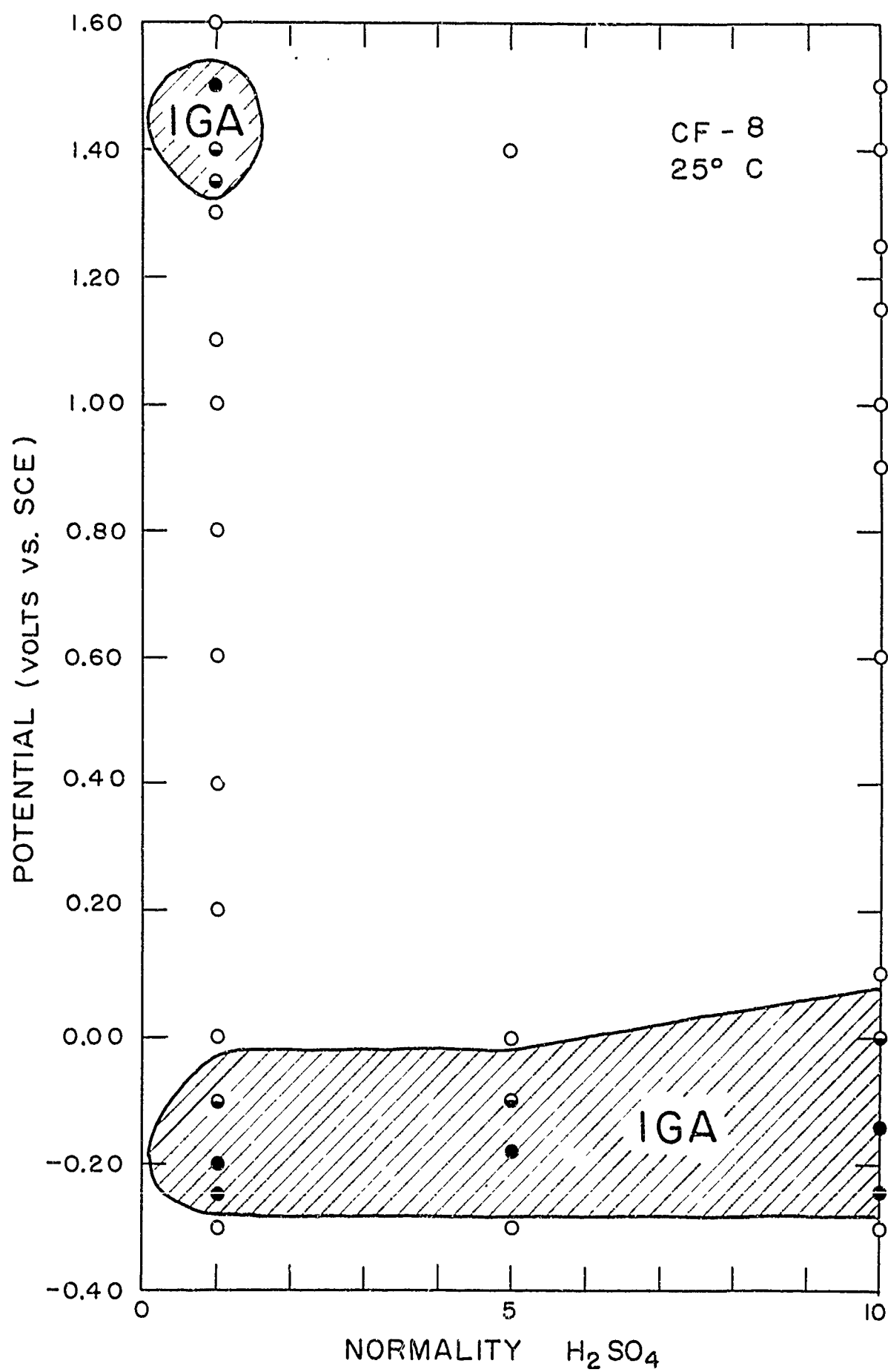


FIG.1

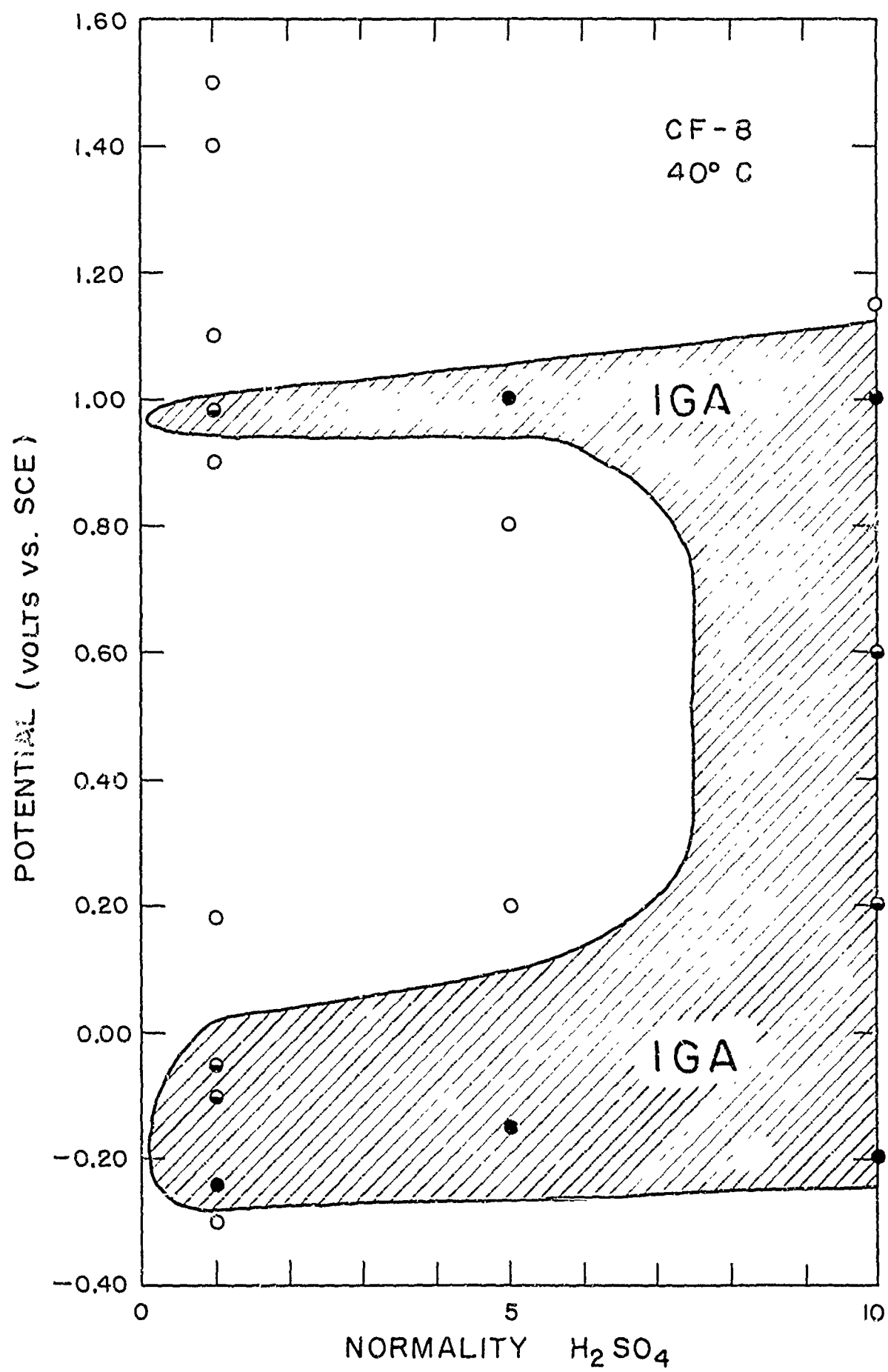


FIG. 2

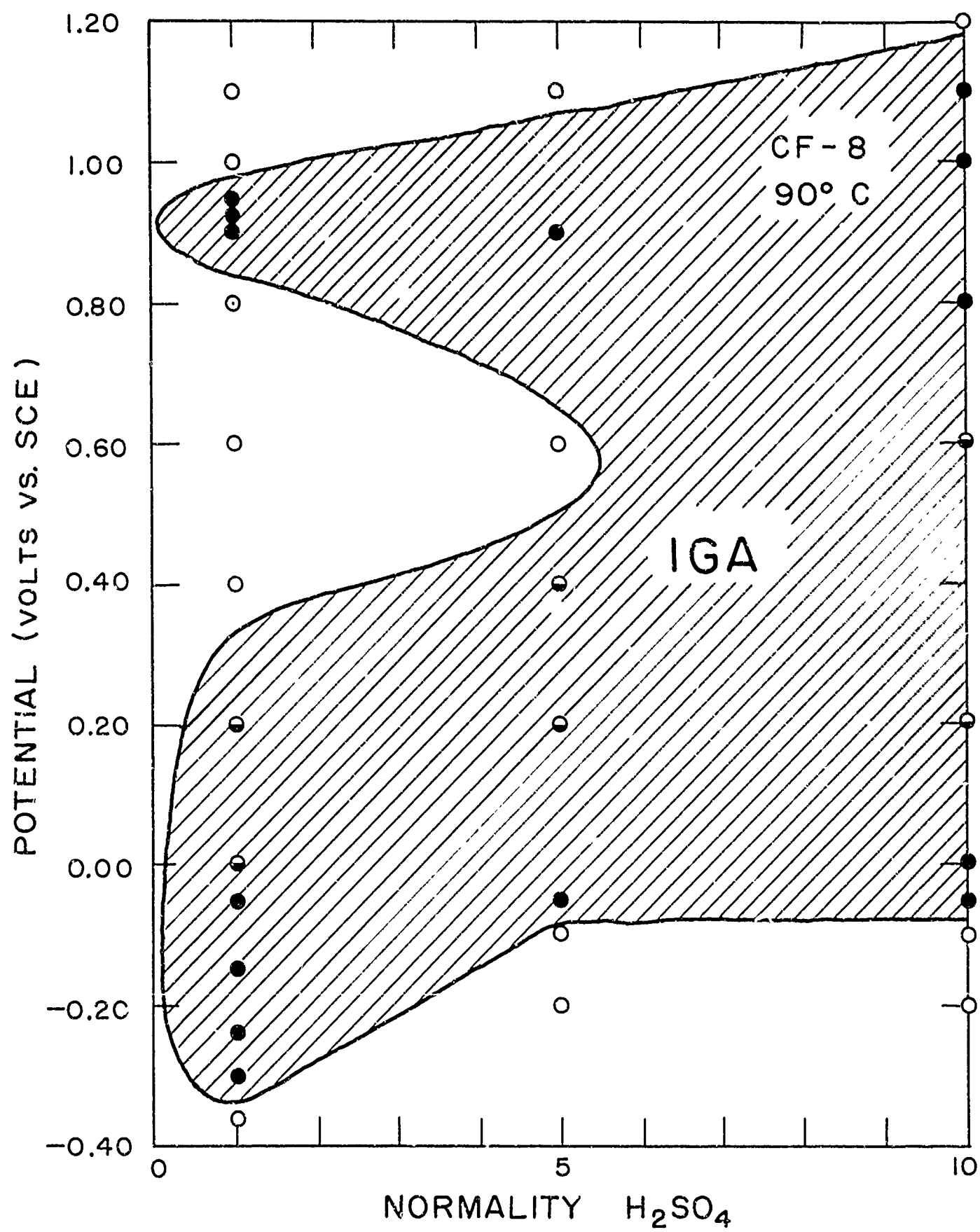


FIG.3

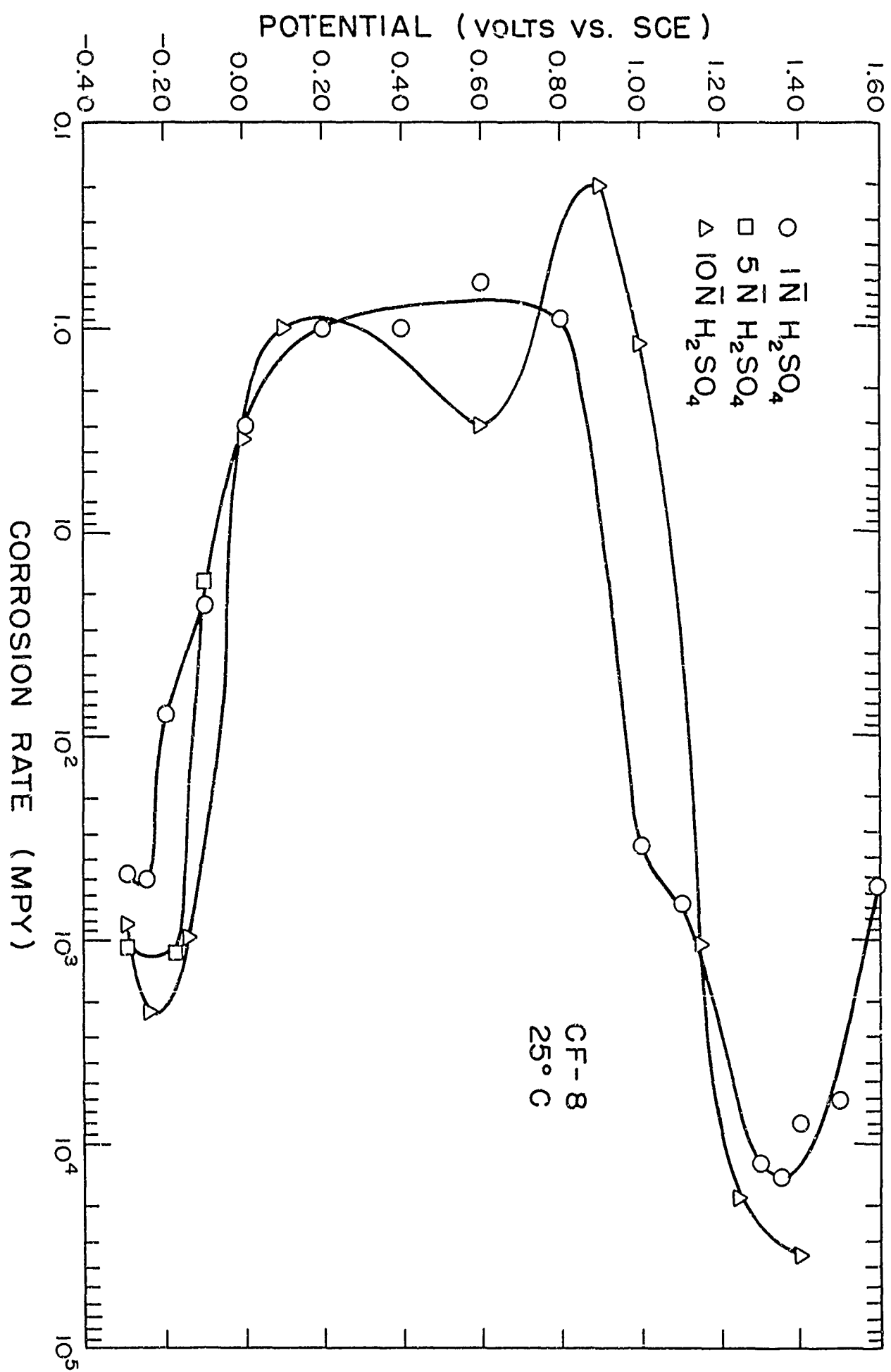


FIG. 4

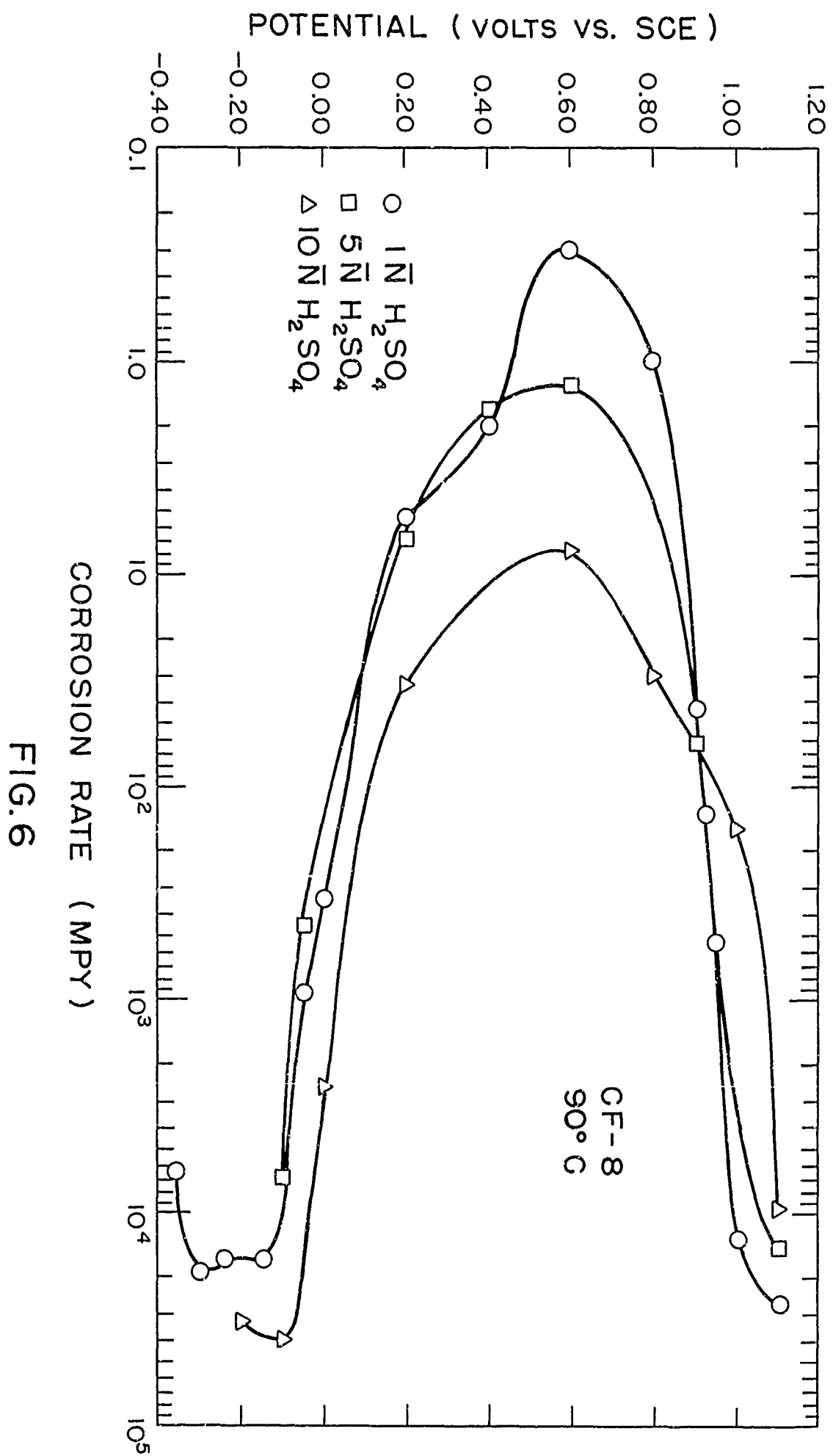


FIG.6

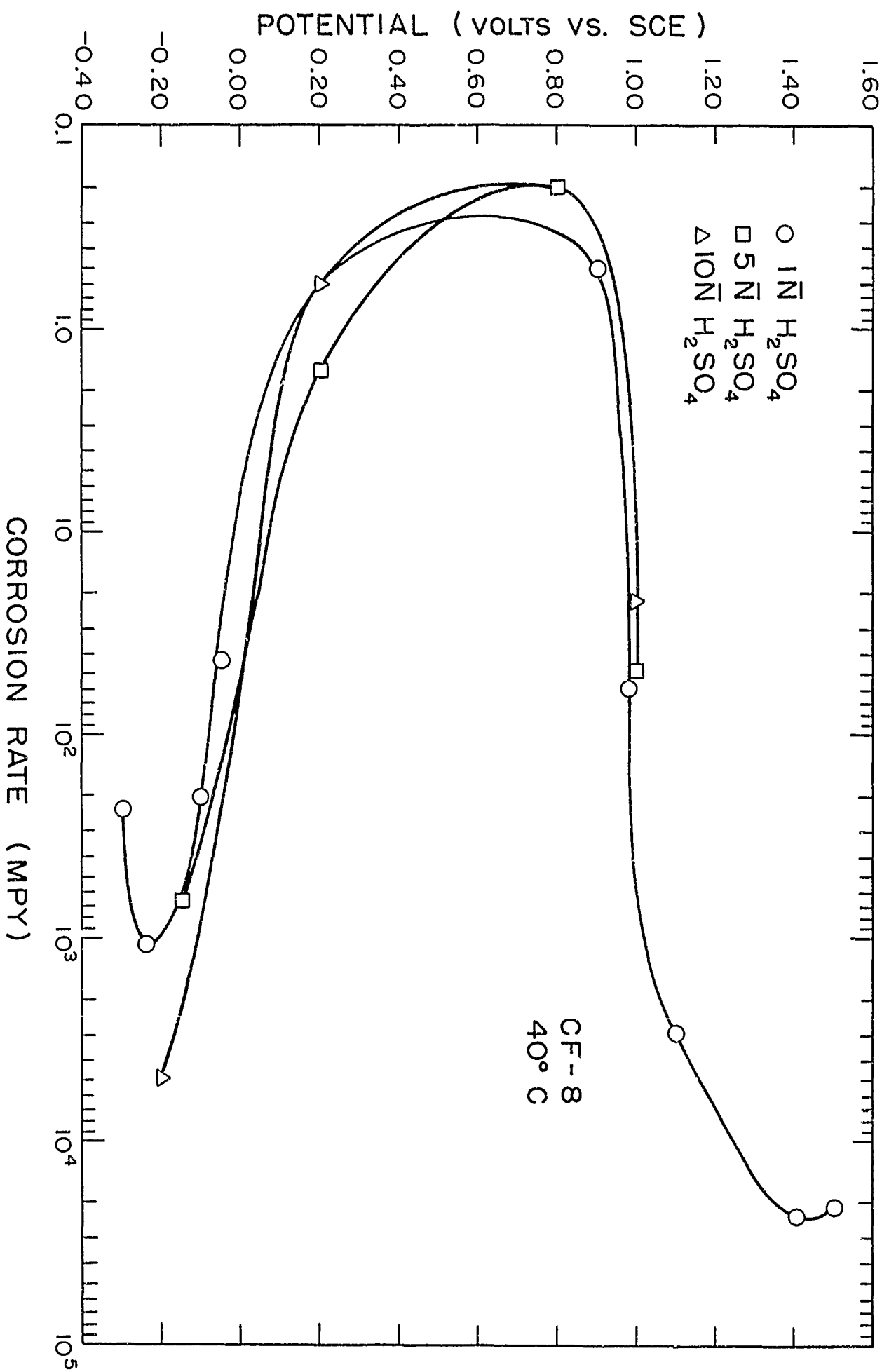
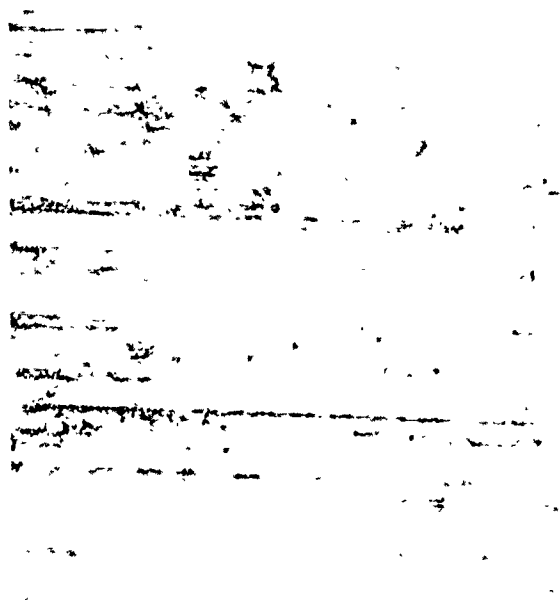


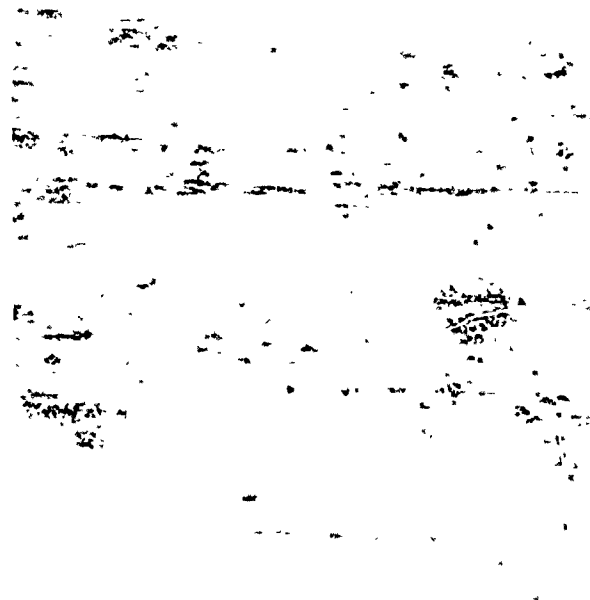
FIG.5

FIGURE 7

	<u>A</u> Controlled Po- tential Test	<u>B</u> Conventional Corrosion Test*
Corrosive Media	10N H_2SO_4	1.0g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per liter 10N H_2SO_4
Solution Temperature ($^{\circ}\text{C}$)	25	25
Immersion Time (hours)	100	98
Specimen Potential (V vs S.C.E.)	0.100	0.24 to 0.25
Corrosion Rate (MPY)	1.0	0.5



A



B

* Test No. 10---see Table III

FIGURE 8

	<u>A</u> Controlled Po- tential Test	<u>B</u> Conventional Corrosion Test*
Corrosive Media	1N H ₂ SO ₄	4.0g. CuSO ₄ .5H ₂ O per liter 1N H ₂ SO ₄
Solution Temperature (°C)	90	90
Immersion Time (hours)	100	100
Specimen Potential (V vs S.C.E.)	0.200	0.23 to 0.25
Corrosion Rate (MPY)	5.4	1.9



A



B

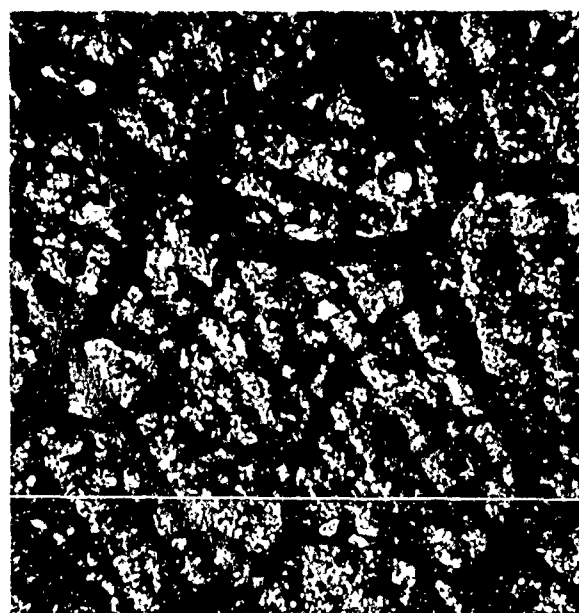
* Test No. 19---see Table III

FIGURE 9

	<u>A</u>	<u>B</u>
	Controlled Po- tential Test	Conventional Corrosion Test*
Corrosive Media	1N H ₂ SO ₄	10g. Ce(SO ₄) ₂ ·4H ₂ O per liter 1N H ₂ SO ₄
Solution Temperature (°C)	90	90
Immersion Time (hours)	100	100
Specimen Potential (V vs S.C.E.)	0.925	0.92 to 0.95
Corrosion Rate (MPY)	130	205



A



B

* Test No. 20 -see Table III